Renewable and Sustainable Energy Reviews 16 (2012) 6717–6724

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Fuel additives from glycerol etherification with light olefins: State of the art

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ARTICLE INFO

Article history:
Received 23 March 2012
Received in revised form
3 August 2012
Accepted 4 August 2012
Available online 5 October 2012

Keywords:
Glycerol
Isobutene
Isoamylenes
Etherification
Biofuels
Ion-exchange resins

ABSTRACT

The production of biofuel has increased considerably over the last years. Glycerol, a by-product of biodiesel synthesis, accounts for 10 wt% of the total product and has a limited range of applications. Etherification reaction of glycerol with light olefins (isobutene, isoamylenes) in liquid phase and catalyzed by acidic macroporous ion-exchange resins could be an attractive solution (i) to address the excess of glycerol, and (ii) to increase the diesel volume using light olefins, obtaining a product of good properties, higher value and especially useful as an additive in diesel and also in biodiesel.

In order to study accurately the etherification of glycerol with isoamylenes, we conducted an extensive literature research to develop our understanding on glycerol etherification with light olefins. We realized that only isobutene without and with solvents and *tert*-butyl alcohol had been investigated experimentally in detail. This paper shows different synthetic routes, raw materials and experimental conditions to obtain good selectivities to ethers and high glycerol conversion.

Contents

1. Introduction

Biofuel is a liquid or gaseous fuel obtained from renewable resources, primarily plant biomass, vegetable oils, and treated municipal and industrial wastes. The main difference between biofuels and petroleum feedstocks is basically its oxygen content [1]. Biofuel production has increased considerably over the last years not only as an environmental measure attempting to reduce air pollution, but also because it improves engine performance [2]. Biodiesel is a type of biofuel consisting of a mixture of different chemicals, which include fatty acid alkyl esters as the main components but also fatty acids or fatty acid monoglycerides [3].

Many countries worldwide (e.g. EU and USA) have enacted legislation aimed at reducing evaporative emissions and regulate complete fuel combustion forcing to produce reformulated gasoline [4]. According to the Directive 2003/30/EC of the European Union, the proportion of biofuels for all the petrol fuels used for transport purposes by the end of 2010 had to be 5.75% [5]. Besides,

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http://dx.doi.org/10.1016/j.rser.2012.08.005

Nomenclature

DEIA	Diether obtained from isoamylene
DEIB	Diether obtained from isobutene
DTAG	Di-*tert*-amyl glycerol ether
DTBG	Di-*tert*-butyl glycerol ether
ETBE	Ethyl *tert*-butyl ether
FCC	Fluid catalytic cracking
FID	Flame ionization detector
FAME	Fatty acid methylic esters
FT-IR	Fourier transform-infrared spectroscopy
FT-Raman	Fourier transform-Raman spectroscopy
GLY	Glycerol
GC	Gas chromatography
GC/MS	Gas chromatograph coupled to mass selective spectrometer
GE	Glycerol ethers
GTAEs	Glycerol *tert*-amyl ethers
GTBEs	Glycerol *tert*-butyl ethers
IA	Isoamylenes
IB	Isobutene
MEIA	Monoether obtained from isoamylene
MEIB	Monoether obtained from isobutene
MTAG	Mono-*tert*-amyl glycerol ether
MTBG	Mono-*tert*-butyl glycerol ether
MW	Molecular weight, g/mol
NMR	Nuclear magnetic resonance
P_c	Critical pressure (MPa)
T_b	Boiling point (K)
T_c	Critical temperature (K)
T_m	Melting point (K)
TAME	*tert*-amyl methyl ether (2-methoxy-2-methyl butane)
TAA	*tert*-amyl alcohol
TAEE	*tert*-amyl ethyl ether (2-ethoxy-2-methyl butane)
TBA	*tert*-butyl alcohol
TEIA	Triether obtained from isoamylene
TEIB	Triether obtained from isobutene
TTAG	Tri-*tert* amyl glycerol ether
TTBG	Tri-*tert* butyl glycerol ether
V_c	Critical volume (cm^3/mol)
ΔG_f^0	Formation Gibbs energy (1 atm; 298 K), kJ/mol
ΔH_f^0	Formation enthalpy (1 atm; 298 K), kJ/mol
2M1B	2-methyl-1-butene
2M2B	2-methyl-2-butene

in accordance with Directive 2009/30/CE [6], reformulated gasoline has to contain a maximum of 3.7 wt% of oxygen as oxygenated compounds (alcohols, ethers), a maximum of 10 ppm of sulphur and a maximum of 18 vol% of olefins. On the other hand, diesel fuel has to comply with the following specifications as per Directive 2009/30/CE: sulphur concentration ≤ 10 ppm, cetane index ≥ 51, polycyclic aromatic hydrocarbons ≤ 8 wt% and FAME (fatty acid methylic esters) ≤ 7 vol%. Notwithstanding these requirements, Member States of the European Union may permit the placing on the market of diesel with a FAME content greater than 7% [6].

1.1. Revaluation of glycerol

A major drawback in biodiesel synthesis is the great amount of by-product obtained, i.e. 1 mol of glycerol (1,2,3-propanetriol) is produced per 3 mol of methyl esters. Glycerol accounts for 10 wt% of the total product [7], which makes the process economically unfeasible. As a result of the excess of production, the price for refined glycerol decreased sharply from €1500 per tonne in 2001 to €330 in 2006 and $400–600 per tonne in 2009 for refined glycerol [8]. Due to the major economic recession that the world is facing nowadays, the biodiesel production in USA was 50% lower in 2009 than in 2008, though worldwide biodiesel capacity was in 2010 a 9% higher than in 2009, which represents 39.8 million ton [8] and the corresponding 3.98 million ton of glycerol. These figures strongly support the need for more effective and environmentally friendly strategies to deal with glycerol.

Glycerol cannot be used as a fuel because of its impurities and the likelihood of oxidation or polymerization at high temperatures, which produces toxic compounds. In addition, the low solubility in hydrocarbons makes it inappropriate as an additive in/to other fuels. Although nowadays glycerol has a limited range of applications, this by-product offers attractive possibilities due to its functional groups (three hydroxyl groups) and can be considered as a valuable resource material to obtain other products with an added high value [9].

A number of processes could be applied to glycerol, which provides evidence of its potential as a raw material [8–11]:

- production of hydrogen and synthesis gas by reforming, pyrolisis and steam gasification,
- production of acrolein, acrylic acid and acrylonitrile by dehydration,
- production of ethylenglycol, propylenglycol and 1,3-propanediol by hydrogenolysis and fermentation,
- selective oxidation to obtain dihydroxyacetone,
- hydrochlorination: Epicerol process to obtain epichlorohydrin,
- carboxylation to produce glycerol carbonate as a source of new polymeric materials,
- esterification and transesterification with fatty acids to produce mono-, di- and tri-glycerides,
- etherification with light (C_4 and C_5) olefins to produce *tert*-butyl and/or *tert*-amyl ethers, and
- telomerisation with 1,3-butadiene to obtain C_8 chain ethers of glycerol.

The derivatives from glycerol etherification with light olefins can be used in fuels even helping to improve biodiesel properties. Oxygenate compounds such as glycerol *tert*-butyl ethers (GTBEs) improve detonation and octane properties of gasoline [1,12] and offer an alternative to oxygenates such as ethyl *tert*-butyl ether (ETBE). The derivates di-*tert*-butylglycerols (DTBG) and tri-*tert*-butylglycerol (TTBG) have shown to be valuable fuel additives to decrease the emission of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes. Such ethers can also act as cold flow improvers in biodiesel, reducing its viscosity [10].

The etherification of glycerol with isobutene to obtain GTBEs (glycerol *tert*-butyl ethers) has few disadvantages, i.e., the product is a mixture of different molecules (mono-, di- and tri-ethers) and isobutene is more expensive than the used glycerol [12]. A number of secondary reactions such as isobutene oligomerization [13] may also reduce the yield of the desired products.

1.2. Revaluation of isoamylenes

The emission of organic volatile compounds (aromatics, sulphur and mainly light olefins) is another main problem that should be considered [14]. Due to their Reid vapor pressure (measure of the vapor pressure of gasoline, volatile crude oils and other volatile petroleum products determined at 38 °C [15])

and their atmospheric photochemical reactivity these compounds are involved in the tropospheric ozone formation [13,16].

The most important contribution of olefin to gasoline (40 vol%) is due to the C_5 olefin fraction obtained from fluid catalytic cracking (FCC), more specifically the isoamylenes (IA): 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) (Fig. 1). These can be found in an average composition of 25 wt% in a typical C_5 stream from a FCC [17]. Isoamylenes are the most problematic fraction in terms of smog and tropospheric ozone, accounting for ≥90% of the total tropospheric ozone formation potential of the gasoline olefins [18]. It is therefore necessary to reduce the content of IA in gasoline and if it is possible, to transform them into more valuable and suitable products with a lower vapor pressure, taking advantage of their reactivity. Different ways can be considered to remove C_5 olefins from gasoline and transform them, such as [19]:

- C_5 alkylation,
- *tert*-amyl methyl ether (TAME) or *tert*-amyl ethyl ether (TAEE) production,
- C_5 isomerization/etherification,
- C_5 hydroformylation/hydrogenation, and
- C_5 oligomerizacion (dimerization and trimerization).

Some of these processes seem to improve fuel properties, e.g., dimerization and trimerization of olefins improve gasoline and diesel quality, respectively [14,16].

TAME production is an example of the use of isoamylenes for etherification purposes. It is obtained by etherification of methanol with 2M2B, 2M1B over an acidic catalyst (see Fig. 2) and it is considered a ''clean'' air additive [20] as it increases the oxygen in the fuel, which reduces the volatility and the quantity of IA present.

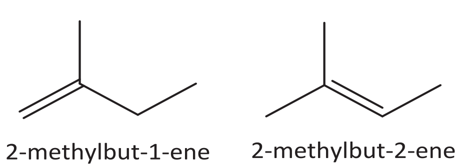


Fig. 1. Molecular structures of isoamylenes.

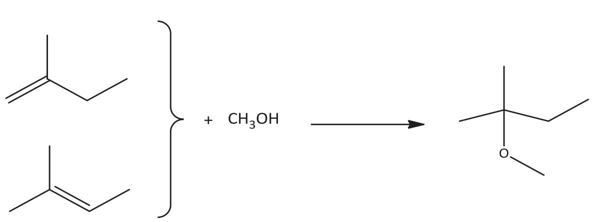


Fig. 2. *tert*-Amyl methyl ether synthesis.

2. Background and state of art

To our knowledge, the physical and chemical properties of ethers from glycerol with light olefins have been poorly addressed in the literature. Therefore, we used a molecular behavior simulation program (Chem & Bio Office Desktop 2010) to predict a number of relevant properties of the discussed ethers. As shown in Table 1, most properties of isobutene-derived and isoamylene-derived ethers do not differ significantly. However, the differences in boiling points are worth noting. MTAG have a $\Delta T_b = 22.88$ K higher than the ethers derived from isobutene. When the triethers are compared, the difference is up to 68.64 K, and this behavior is also seen in other predicted properties. Ethers derived from IA have higher boiling, melting and critical temperatures, and higher critical volumes and formation Gibbs energy, which can be attributed to their heavier molecular weights. IA-derived ethers have the lower critical pressure and formation enthalpy than those derived from isobutene, which suggests that their formation is more exothermal than for ethers derived from isobutene. Thus, the energy demand to form MTAG, DTAG and TTAG is lower. Nevertheless, the prediction of the formation Gibbs energy shows that the formation reaction of IA ethers is less spontaneous, which could be solved modifying the working temperature. If the predicted properties of ethers derived from isoamylenes are compared, it is apparent that the boiling and melting points and the critical temperature increase with the molecular weight. The critical volume and the formation Gibbs energy also rise while the critical pressure and the formation enthalpy decrease with the molecular weight increase. It can be observed that the formation of the MTAG is thermodynamically more spontaneous ($\Delta G_f^0 = -361.76$ kJ/mol) than the formation of the DTAG ($\Delta G_f^0 = -285.00$ kJ/mol) or the TTAG ($\Delta G_f^0 = -208.24$ kJ/mol), as it could be expected due to steric hindrance.

Only one study (Noureddini's patent) dealing with the etherification of glycerol with isoamylene has been published so far [21]. Unfortunately, no accurate data of experimental conditions, glycerol conversion, selectivity and yield were found but from the point of view of the organic synthesis, five ethers (two monoethers, two diethers and one triether) are expected to be formed (see Fig. 3). Nevertheless, some studies have been published in the literature investigating *tert*-butyl etherification of glycerol. When glycerol is etherified with isobutene (see Fig. 4) five ether isomers can be expected: two monoethers (3-*tert*-butoxy-1,2-propanediol and 2-*tert*-butoxy-1,3-propanediol), two diethers (2,3-di-*tert*-butoxy-1-propanol and 1,3-di-*tert*-butoxy-2-propanol) and one triether (1,2,3-tri-*tert*-butoxy propane). In addition, some secondary reactions can take place, which must be minimized: the formation of *tert*-butyl alcohol (TBA) in the presence of traces of water and the oligomerization of isobutene to C_8, C_{12} and C_{16} olefins [22].

Guerrero-Pérez et al. [9] showed that these diethers or triether formed from isobutene have good burning characteristics (similar to traditional oxygenates like MTBE, ETBE, etc.) and that added to gasoline or to diesel they can decrease the emissions of particulate matter, hydrocarbons, carbon monoxide and unregulated

Table 1
Physical and chemical properties of ethers derived from isobutene and isoamylene with glycerol.

	MW	T_b	T_m	T_c	P_c	V_c	ΔG_f^0	ΔH_f^0
MEIB	148.20	562.87	299.41	668.15	3.477	466.55	−370.18	−638.32
MEIA	162.23	585.75	310.71	683.92	3.114	522.50	−361.76	−659.16
DEIB	204.31	581.40	308.35	678.13	2.124	678.50	−301.84	−709.82
DEIA	232.36	627.16	330.89	707.56	1.792	790.50	−285.00	−751.10
TEIB	260.41	599.93	317.26	688.24	1.430	890.50	−233.50	−781.12
TEIA	302.49	668.57	351.07	729.24	1.163	1058.50	−208.24	−843.04

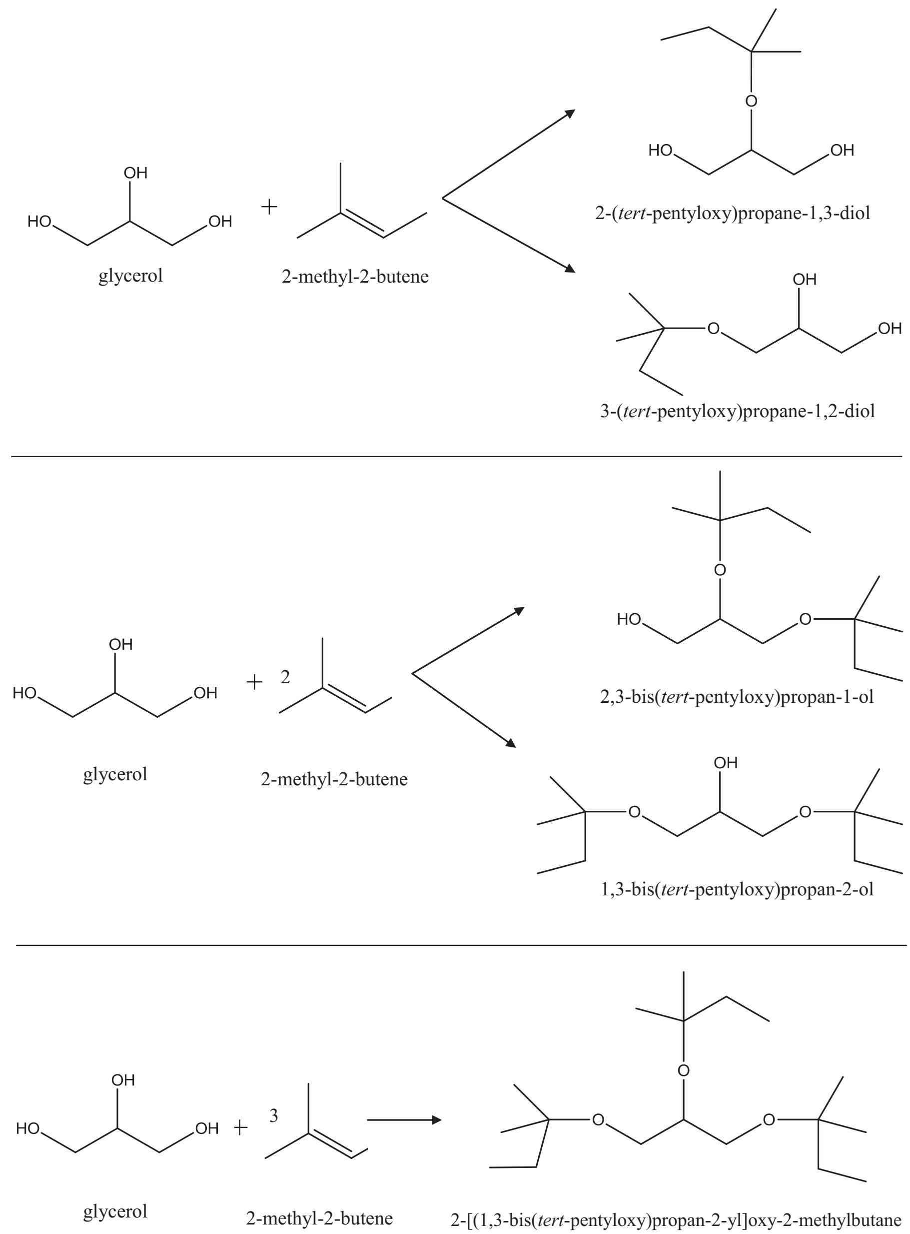


Fig. 3. Glycerol etherification with isoamylenes.

aldehydes. Moreover, their addition to diesel reduces its viscosity and improves its cold flow[1].

In the literature, experiments are performed using either homogeneous or heterogeneous catalysts. The use of the homogeneous catalysts is not advisable for a number of reasons [5]. Their acidic characteristics may induce corrosion in the equipment, while the impossibility of recovering the catalyst makes this option non-viable [13]. By contrast, heterogeneous catalysts can be easily recovered from the reaction mixture by decantation or filtration for further reuse.

2.1. Etherification of glycerol with isobutene without and with solvents

Karinen and Krause [7] studied this reaction using an ion-exchange macroreticular resin catalyst (Amberlyst 35). A 50 cm^3 batch reactor with a mechanical stirrer was used, which included a mixing baffle and a basket where the catalyst was placed. In order to increase the selectivity towards glycerol ethers (GE) and hinder isobutene oligomerization, near stoichiometric ratio of glycerol and isobutene and temperatures above 343 K were required. The optimal conditions for the formation of ethers were 353 K with an initial isobutene/glycerol ratio of 3, 1.5 MPa of pressure and a reaction time of 7 h. At low stirring speeds, <1000 rpm, more oligomerization occurred, while at higher stirring speeds more selectivity towards ethers was obtained. The chosen stirring speed was 1300 rpm. Samples were analyzed with a gas chromatograph equipped with a HP-Innowax column ($30\ m \times 0.25\ mm \times 0.250\ mm$) and a FID. The reaction products were identified by GC/MS. Initially, two phases were formed in the reaction mixture due to the insolubility of isobutene and glycerol in each other. The reaction products were accumulated in one or other phases according to their solubility. Thus, monoethers, more polar, were mainly solved in the glycerol phase, while diethers, triether and C_8–C_{16} were more concentrated in the non-polar phase. However, all components were present in some

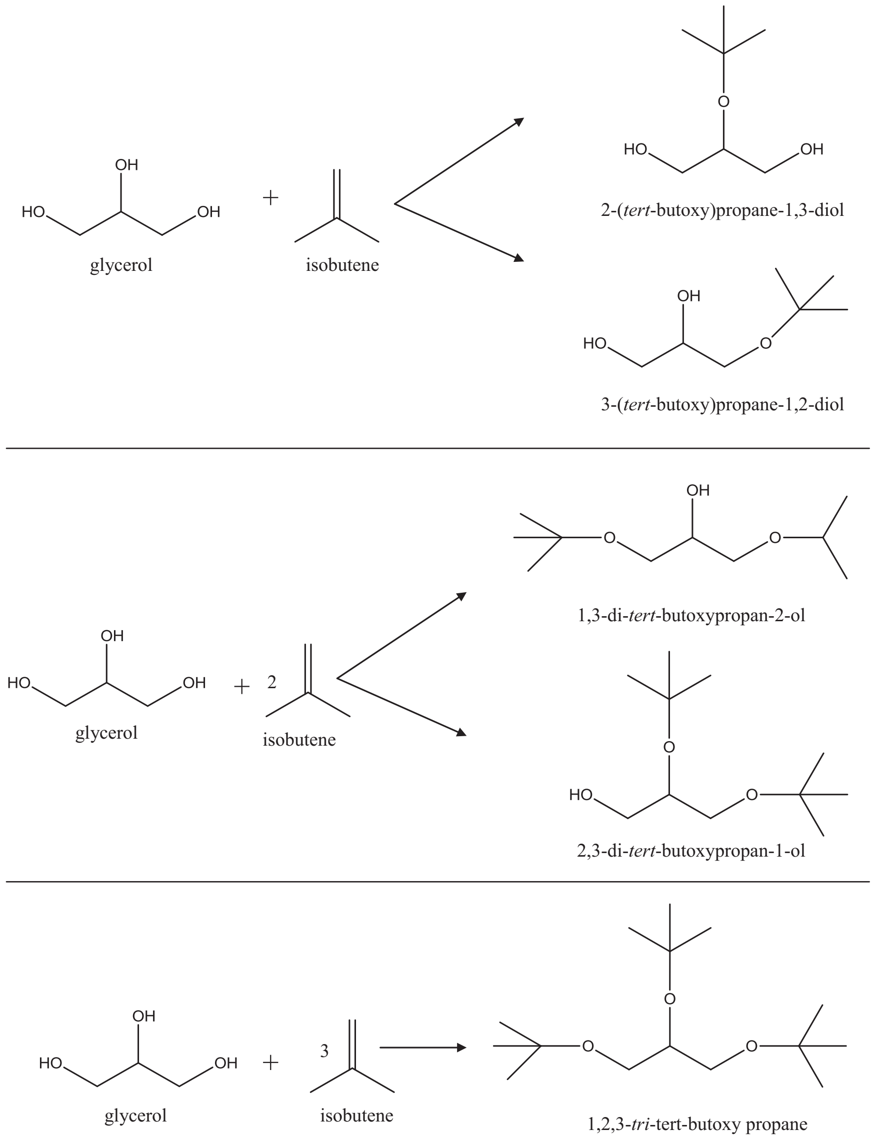


Fig. 4. Glycerol etherification with isobutene.

degree in both phases. When the conversion of glycerol was about 60–70%, the two phases dissolved in each other and only one phase remained.

Karinen and Krause also found that viscosity affects mass transfer between the different phases and the catalyst [7]. Greater glycerol contents in the reaction mixture (low initial IB/GLY ratios) increased the viscosity and reduced the reaction rates, while an excess of isobutene favoured the oligomerization reaction. These authors also noticed that the addition of *tert*-butyl alcohol to the reaction mixture hinders the oligomerization of isobutene and the mass transfer limitations are reduced.

Melero et al. [5] synthesized a propylsulfonic-acid-functionalized mesostructured silica (Pr-SBA-15) and an arenesulfonic-acid-functionalized mesostructured silica (Ar-SBA-15) as catalysts and compared them to Nafion-SiO_2 composite (SAC-13) (with resin content in the range of 10–20 wt%), commercial Purolite CT-275 and acidic macroporous resins (Amberlyst 15 and Amberlyst 36). Optimal experimental conditions were found at 348 K, an IB/GLY molar ratio of 4/1 with a catalyst loading of 5 wt% (referred to glycerol mass) and stirring speed = 1000 rpm. Reaction samples were analyzed by GC (Varian 3900 chromatograph) using a CP-WAX 52 CB column (30 m × 0.25 mm, DF = 0.25) and a FID detector. The study demonstrated that (i) sulfonic acid-functionalized mesostructured silicas are excellent catalysts in the etherification of glycerol with isobutene and (ii) if used with a silica matrix, isobutene oligomerization was reduced and higher production of diethers and triether was obtained. In addition, they noticed that the acid strength of the catalysts seems to be an influential parameter in the catalytic performance. The use of moderately strong acid centers improved the results obtained both in glycerol conversion and selectivity towards the desired products. However, they also noticed that at high temperatures, more monoether was obtained due to the increase of dealkylation of DTBG (di-*tert*-butyl glycerol) and TTBG (tri-*tert*-butyl glycerol).

Another relevant research was carried out by Klepáčová et al. [23] with the main purpose of comparing the use of different macroporous and microporous ion exchange resins (Amberlysts 15, 35, 36, 39, 31 and 119) and zeolites (H-Y and H-Beta). At a stirring frequency of 1200 min^{-1}, the influence of external mass transfer was negligible, and therefore this was used in all experiments. Samples of reaction products were analyzed on capillary column HP-Innowax (30 m × 0.32 mm × 0.5 μm) in a gas chromatograph CHROM 5. The temperature of the analysis was increased from 313 to 493 K (with a slope of 10 K min^{-1}) and for 5 min it

was maintained under isothermal conditions at 493 K. The highest yield of di- and tri-ethers and the highest conversion of glycerol were obtained at 333 K on Amberlyst 35. Large pore zeolites provided lower selectivity than ion-exchange resins. They also concluded that (i) etherification was preferred on primary hydroxyl groups; (ii) the presence of water inhibited the catalyst and (iii) the increase in temperature results in an increase of secondary reactions such as disproportionation of glycerol ethers and dimerization of isobutene.

Some years later, Klepáčová et al. [13] studied the reaction again using other different catalysts paying special attention to the influence of temperature on the reaction. They proposed a kinetic model for the etherification reactions. Reactions were carried out in the temperature ranges from 323 to 363 K in the presence of solvent (dioxane). The samples were analyzed on capillary column HP-Innowax (30 m × 0.32 mm × 0.5 μm) in a gas chromatograph CHROM 5 with a temperature program from 313 to 493 K (with a slope of 10 K min^{-1}) and at 493 K for 5 min isothermally. They demonstrated that *tert*-butylation of glycerol is a set of acid catalyzed consecutive equilibrium reactions and the existence of two independent side reactions which are considered as undesired: oligomerization and hydratation of isobutene. Zeolites were not convenient as catalysts because of their easy deactivation and higher price than ion-exchange resins. The highest conversion of glycerol on Amberlyst 35 (71.5%) was achieved at 333 K after 180 min of reaction. At higher temperatures and longer reaction times, the undesired isobutene dimerization became the most important reaction. On the other hand, three solvents were compared for etherification reaction of ethylene glycol with isobutene: dioxane, sulfolane and dimethyl sulfoxide. The highest conversion was reached using dioxane as solvent, and they concluded that the solvent could affect the etherification reaction. The kinetic study of glycerol etherification was carried out using dioxane as solvent.

Xiao et al. [24] recently improved the catalytic performance of a commercial zeolite HY by means of an adequate treatment with citric or nitric acid. This treatment led to increase the surface area, pore size and pore volume of catalyst which results beneficial to the conversion of glycerol to DTBG and TTBG. At 343 K with 1 wt% catalyst loading, the glycerol conversion and the selectivity to DTBG and TTBG after 7 h were 85% and 58%.

Lee et al. [22] also set out to compare different catalysts for *tert*-butyl etherification of glycerol. The most active catalyst per weight basis was fine powder of Amberlyst-15, but this catalyst involved a large obtaining of isobutene dimers. Before the experiment, the reactor was flushed with nitrogen and adjusted to 2.0 MPa when introducing liquid isobutylene. In typical runs, the conditions used were: 11.50 g (0.125 mol) of glycerol, 0.86 g dry catalyst (7.5 wt%/ glycerol), 28.2 g (0.503 mol) isobutylene; 333 K; 1200 rpm (above 1000 rpm the product distribution does not depend on stirring speed). To avoid the secondary reaction, the catalyst was modified using a partial exchange of acidic protons with suitable metal cations, leading to the suppression of isobutene oligomerization and changing the product distribution of glycerol ethers. Standard analysis of all the components was performed in an Agilent 7890 System equipped with Agilent DB-WAX column (30 m × 0.32 mm × 0.25 μm) and 1-octanol was used as internal standard.

Another active catalyst for the etherification reaction of glycerol with isobutene was described by Zhao et al. [25]. This consists of a carbon-based catalyst prepared from partially carbonized peanut shell. With a molar ratio of 4:1 (isobutene/glycerol), a catalyst-to-glycerol mass ratio of 6 wt%, a reaction temperature of 343 K and a reaction time of 2 h, glycerol was completely transformed into a mixture of glycerol ethers, including mono-*tert*-butylglycerols (MTBGs), di-*tert*-butylglycerols (DTBGs) and tri-*tert*-butylglycerol (TTBG) and the selectivity toward the sum of the desired DTBGs and TTBG of 92.1% was obtained. The samples of reaction products were analyzed in an Agilent 4890D gas chromatograph, with an HP-Innowax column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector.

Di Serio et al. [12] evaluated the use of Amberlyst 15 as catalyst for the direct synthesis of glycerol *tert*-butyl ethers (GTBEs) from isobutene and glycerol and used two new processes to extract ethers with biodiesel. The best performances in terms of conversion and selectivity were obtained under reaction time of 480 min, molar isobutene/glycerol ratio = 2, $T = 363$ K and 500 rpm stirring rates. Higher isobutene/glycerol ratios and/or temperatures favor the formation of oligomers. In both separation schemes, GTBEs are extracted using biodiesel as the extracting agent. In the first very simple scheme, a final product with a glycerol content greater than that required by the EN14214:2003 specification was obtained, while in the second scheme, an additional washing step with water lowered this value to the desired level. The first process allowed them to obtain about 7.5% of GTBEs in the mixture biodiesel/GTBEs, but the content of glycerol exceeded the specifications. The second process with a washing step with water results into a similar content of GTBEs while the final concentration of glycerol is $\leq 0.02\%$, in agreement with the specification. Therefore, this product can be used as the biodiesel additive.

Voicu et al. [26] showed that the heteropolyacid $H_4SiW_{12}O_{40} \cdot 30H_2O$ was a performant catalyst for glycerol etherification. The experiments were carried out in discontinuous mode at 353 K during 5 h at 1200 rpm using an initial molar ratio IB/Glycerol of 3. Characterization of reaction products was performed by gas-chromatography with FID detector equipped with DB-WAX polar column. High conversion of glycerol (93,6%) and high yields to ethers (around 38.1% of MTBG, 52.2% of DTBG and 3.3% of TTBG) were obtained. To improve the mass transfer between phases, three emulsifiers were employed: amphoteric ammonium quaternary salt C19, non-ionic ethoxylated alcohol C_{12}–C_{14}, and cationic Dinoram S. The amphoteric ammonium quaternary salt C19 at 0.7% concentration has been the most efficient emulsifier because the formation of direct emulsion favors total conversion of glycerol, also providing the highest yields to the desired products di- and tri-ethers (about 56.1% of DTBG and 33.1% of TTBG).

With regard to the identification of mono, di and tri *tert*-butyl ethers of glycerol, Jamróz et al. [27] used different methods such as GC, GC–MS, NMR, FT-IR and FT-Raman which allowed not only their identification but also their quantification.

2.2. Etherification of glycerol with tert-butyl alcohol

The etherification of glycerol with *tert*-butyl alcohol (TBA) has been also covered in the literature. Frusteri et al. [28] investigated the etherification with *tert*-butyl alcohol in presence of silica supported acid catalysts. Experiments were performed at 1.0 MPa in a batch reactor with temperature ranging from 303 to 363 K under stirring frequency of 1200 rpm, in order to limit the influence of external mass transfer phenomena. Reaction times ranged from 1 to 30 h, and TBA/glycerol ratios from 2 to 5 and using a catalyst-to-glycerol weight ratio of 0.3 to 7.5 wt%. In addition to the silica catalysts, the ion-exchange resin A-15 was used to evaluate the influence of experimental parameters owing to its higher acid capacity. The liquid reaction mixture after reaction was analyzed off-line by a gas chromatograph, HP 6890N, equipped with a capillary column HP Innowax under the following oven temperature program: from 313 to 493 K (20 K min^{-1}) and at 493 K for 3 min. Although glycerol conversion increased with reaction temperature, no full conversion into

alkyl ethers was achieved (95% after 6 h with A-15) into alkyl ethers due to de-etherification reactions. Only four of five expected ethers were observed, as no tri-substituted ether was formed across the whole range of temperatures. Regarding the amount of catalyst used, they observed a significant increase in the glycerol ether formation with the increasing amount of catalyst from 0 (no reaction) to 7.5 wt%. In terms of reaction time, the concentration of monoethers decreased while the concentration of diethers increased as the reaction proceeded. On the other hand, it was observed a certain amount of isobutene arisen from *tert*-butanol dehydration. However, the formation of oligomers was not observed since the presence of water limits the extent of oligomerization.

Ozbay et al. [29] performed this reaction using different catalysts. The *tert*-butyl alcohol/glycerol molar ratio was adjusted to 8/1, and experiments were carried out at different temperatures depending on the catalyst in a tubular fixed bed reactor. For Amberlyst-15, A-16 and A-35, temperature range was between 353 and 383 K; 353 and 473 K for Nafion-SAC-13 and 423 and 673 K for γ-Al_2O_3. Samples were analyzed with a gas chromatograph (Agilent 6890N), with a FID and a capillary HP Innowax column. Significant increase of conversion was observed with the increasing temperature, for acidic ion exchange resins. Among the Amberlyst type catalysts, A-15 yielded the highest activity. A conversion level of about 50% observed at 383 K is quite high, considering the short residence time of about 20 s in the flow reactor. Alumina showed extremely low activity and only monoethers were found. Diether selectivity reached the highest value (31%) in presence of A-16 at 373 K, though the activity order of the acidic macroreticular resins was A-15 > A-35 > A-16. The authors concluded that due to the large size of glycerol molecules, macroporous catalysts have higher activity than other solid acid catalysts with smaller pore size. The main inconvenient is that using *tert*-butyl alcohol as a reactant, the amount of monoethers and diethers obtained is higher than using isobutene while the quantity of triether is lower, because of the formed water in the reaction with *tert*-butyl alcohol inhibited the catalysts.

A systematic optimization on the etherification of glycerol with TBA was conducted by Chang and Chen [30] using the rbfSolve routine in TOMLAB/CGO. This was aimed at investigating the operating conditions that maximized the yield of mono- and diethers (MTBG and DTBG). The experiments were carried out during 8 h using 35 mL of reacting mixture under at stirring frequency of 1250 rpm to avoid the external mass transfer influence. Amberlyst-15 was used as catalyst and a TBA/GLY molar ratio of 4. Several conditions were studied: temperatures 333–373 K, catalyst 2–10 wt% and different percentages (0–30%) of n-hexane as solvent. The optimal operating conditions were $T=362.4$ K, 7.3 wt% catalyst and in the absence of *n*-hexane. Glycerol conversion reached 72.3% with the product yields of 0.509 mol MTBG and 0.205 mol DTBG per mole of glycerol.

A research that determined the kinetic model parameters for the etherification of glycerol with TBA was undertaken by Kiatkittipong et al. [31]. This paper presents a thermodynamic analysis to determine the equilibrium composition and the kinetic model parameters. The experiments were carried out into an autoclave reactor during 8 h at catalyst weight = 1.025 g, glycerol/TBA = 1:4, pressure = 0.5 MPa and a temperature range of 338–358 K. The samples were analyzed by a gas chromatography (GC 14B, Shimadzu Corp.) employing a capillary column of HP- Innowax (30 m × 0.32 mm × 0.5 m). The temperatures of the injector and the detector were 573 and 423 K, respectively. The temperature programmed was applied by setting the initial column temperature at 313 K with the ramping rate of 10 K min^{-1} to the final column temperature of 513 K and holding for 5 min. Simulations of the etherification of glycerol and TBA in the reactive distillation (RD) were carried out using the RADFRAC model in the Aspen Plus to find the optimal reactive distillation process configuration. The simulation results are compared with experimental data. Thus, the estimated equilibrium conversion showed good agreement with the experimental data reported by Klepáčová et al. [23,32]. A Langmuir–Hinshelwood activity based model, which includes the effect of water adsorption, was found to be the best kinetic model to fit the experimental results.

A novel route to synthesize *tert*-butyl ethers of glycerol from epichlorohydrin was described by Al-Lal et al. [33]. Epichlorohydrin is a raw material mainly used to yield epoxy resins and it is mainly obtained from propylene, although Solvay has recently developed a process to obtain epichlorohydrin from glycerol [10]. This paper reports a three-step route:chlorohydrin ether, glycidyl ether and 1,3-di-*tert*-butoxypropan-2-ol synthesis respectively to transform epichlorohydrin (obtained from glycerol) reacting with *tert*-butanol to obtain mainly DTBG. Conversion is almost quantitative; however yield decreased ≈25% in each step. Among the four catalysts tested for the synthesis of DTBG compound, boron trifluoride etherate provided the best results because it gave better yield and selectivity values, at the same quantitative conversion.

3. Conclusions

This review provides an extensive look at the glycerol etherification with light olefins to convert glycerol into a biodiesel additive and also to transform volatile compounds (isobutene, isoamylenes) into others with lower vapor pressure in order to (i) minimize environmental problems, (ii) find new ways to increase the production of diesel fuel and (iii) find a solution to the surplus of glycerol and transform it in a revaluated product.

Ion exchange resins have been reported throughout the literature to be good catalysts for glycerol etherification with isobutene. Good selectivities to ethers and glycerol conversion have been obtained with them. On the other hand, the presence of solvents, mainly 1,4-dioxane, improves the mass transfer between glycerol and isobutene and better glycerol conversion values have been observed. Using TBA instead of isobutene avoids the secondary reactions like isobutene oligomerization and the selectivities to MTBG and DTBG increase. However, the selectivity to triether decreases significantly as the water produced from *tert*-butyl alcohol decomposition inhibits the catalyst. These studies about the etherification of glycerol with isobutene or TBA can be extrapolated to the etherification of glycerol using isoamylenes as olefins or *tert*-amyl alcohol (TAA) and acidic ionic exchange resins as catalysts.

The predicted properties of ethers derived from isoamylenes shows that an increase in the molecular weight of the ethers results in an increase in the boiling and melting points, the critical temperature, the critical volume and the formation Gibbs energy, while the critical pressure and the formation enthalpy decrease. In addition, the similarity between the properties of ethers derived from isobutene and the predicted properties of ethers derived from isoamylenes also allow the prediction of the reaction behavior with good conversion values and selectivities to diethers and triether derived from isoamylenes. Moreover, good applications for its products are expected, especially the use as additives in diesel and biodiesel.

Acknowledgments

This work was supported by funds of the Science and Innovation Ministry of Spain in the 6th National Research Plan I+D+i 2008–11, through the Subprogram of unguided Basic Research Projects, Project CTQ2010-14796, subprogram PPQ.

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